

Unforeseeable Processes in the Systems Containing Strongly Basic Cross Linked Ionic Polymer and $\text{Fe}_2(\text{SO}_4)_3$ Solution

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Abstract

It was found, that in the system containing $\text{Fe}_2(\text{SO}_4)_3$ solution and strongly basic anion exchanger redox processes take place, with formation of Fe^{2+} ions and nitrogen containing compounds. The processes of Fe^{2+} ions and nitrogen compounds (NO_2^- , NO_3^-) formation in the system are influenced by many factors studied in this paper ($\text{Fe}_2(\text{SO}_4)_3$ and Na_2SO_4 concentration, temperature, pH of solution, speed of air bubbling through the solution, polymer mass, duration of polymer contact with solution). To evaluate the influence of these factors a response surface methodology was used. Optimization of the NO_3^- formation process was carried out by using the method of movement along the gradient.

Keywords

Anion Exchanger; Iron; Nitrate; Redox Processes; Response Surface Methodology

Introduction

In the systems, containing strongly basic anion exchanger and solution of some electrolytes, besides anion exchange processes formation of solid metal compounds can take place in the polymer phase. As known, strongly basic cross-linked polymers do not contain negatively charged or electron donor atoms in their matrix and, theoretically, they cannot interact with metal cations. However, in certain conditions, in $\text{M}_2(\text{SO}_4)_3$ solutions, where M is Fe^{3+} , Al^{3+} or Cr^{3+} , they can interact with metal cations. The retention of cations by these polymers takes place through the formation in their phase of jarosite mineral-type compounds: $\text{R}_4\text{N}[\text{M}_3(\text{OH})_6(\text{SO}_4)_2]$ and $\text{H}_3\text{O}[\text{M}_3(\text{OH})_6(\text{SO}_4)_2]$, where R_4N^+ are functional groups of the polymer. Being modified with metal compounds, strongly basic resins become selective sorbents and catalysts. Recently it was observed that in the systems, containing strongly basic resins and solution of three-charged metallic cations, besides anion exchange and formation of the

jarosite mineral type compounds, complicated redox processes take place with formation of nitrogen compounds.

Experimental Procedures

The commercial strongly basic anion exchanger AV-17 in Cl-form has been used. The exchanger is gel-type cross linked polymer with $-\text{N}^+(\text{CH}_3)_3$ functional groups. Its full anion-exchange capacity is 3.5-4.0 meq./g. The solutions were prepared using $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ salt. To evaluate the influence of different factors (concentration of $\text{Fe}_2(\text{SO}_4)_3$ and Na_2SO_4 , temperature and pH of solution, speed of air bubbling through the solution, polymer mass and duration of the polymer contact with solution) on Fe(III)-containing cations sorption, Fe^{2+} , NO_2^- and NO_3^- ions formation, the response surface methodology (G.E.P.Box and K.B.Wilson method) was used. The experiments were carried out according to matrix of Fractional Factorial Experiment plan. The influence degree of factors on the studied processes was expressed by the regression equations which were calculated according to the reference. The Student criterion of the coefficients significance in the regression equations (b_{sig}) was calculated at a level of significance of 5% and number degree of freedom $f=7$. The optimization of the process of NO_3^- formation was carried out by using method of movement along the gradient. The Fe^{3+} and Fe^{2+} ions content in the polymer phase were determined photocolorimetrically after desorption. Nitrite ions were determined photocolorimetrically using the Griess reactive, while nitrate ions were determined by the potentiometric method with an ion-selective electrode.

Results and Discussion

As seen in Figure 1, the sorption of Fe^{3+} ions depends considerably, while the time of the sorption

equilibrium establishment does not depend on $\text{Fe}_2(\text{SO}_4)_3$ concentration. As it was mentioned above, the processes, which take place on polymers contacting with electrolyte, depend on many factors. The researched factors are shown in the Table 1:

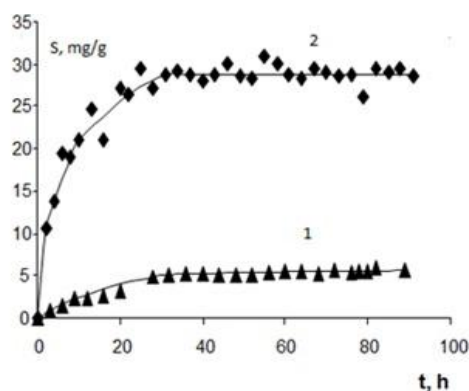


FIGURE 1 KINETIC CURVES OF Fe(III)-CONTAINING CATIONS SORPTION AT 50°C ON AV-17(Cl) FROM SOLUTION WITH 1g/ AND 4g/L OF $\text{Fe}_2(\text{SO}_4)_3$

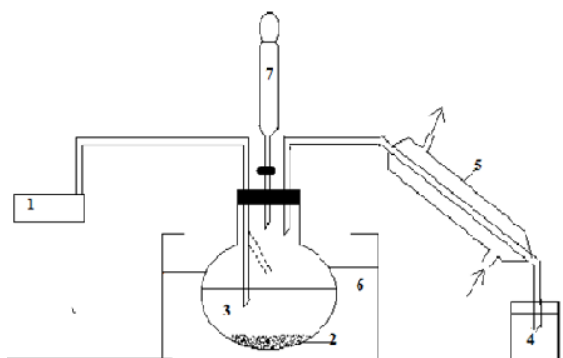


FIGURE 2 EXPERIMENT INSTALLATION: 1 – AIR PUMP, 2 – POLYMER AV-17(Cl), 3 – SOLUTION OF $\text{Fe}_2(\text{SO}_4)_3$, 4 – CONTAINER WITH DISTILLED WATER, 5 – CONDENSER, 6 – THERMOSTAT, 7 – SEPARATING FUNNEL

The experiments were carried out based on the matrix of a Fractional Factorial Experiment (Tab. 2.) using the installation shown in Figure 2.

The following responses of the system were measured and calculated:

- Y_1 – total content of iron ions ($\text{Fe}^{3+} + \text{Fe}^{2+}$) in the polymer phase, (mg Fe/g);
- Y_2 – content of Fe^{2+} ions in the polymer phase, (mg Fe^{2+} /g);
- Y_3 – content of Fe^{3+} ions in the polymer phase, (mg Fe^{3+} /g);
- Y_4 – content of NO_2^- ions in water (in recipient on Figure 1), (mg NO_2^- /g);
- Y_5 – content of NO_3^- ions in water, (mg NO_3^- /g);
- Y_6 – pH of water;
- Y_7 – content of NO_2^- ions in solution of $\text{Fe}_2(\text{SO}_4)_3$, (mg NO_2^- /g);
- Y_8 – content of NO_3^- ions in solution of $\text{Fe}_2(\text{SO}_4)_3$, (mg NO_3^- /g);
- Y_9 – content of NO_2^- ions in the polymer phase, (mg NO_2^- /g).

The results (Tab.2.) were the averages of two independent experiments. The obtained results were used for calculation of the coefficients of the regression equations (1)–(9) according to:

$$Y_1 = 28.31 + 7.93X_1 + 9.17X_2 + 8.11X_3 - 4.15X_4 - 1.085X_5 - 1.05X_6 + .93X_7 \quad b_{\text{sig}} = 0.945; \quad (1)$$

$$Y_2 = 0.317 + 0.298X_1 + 0.055X_2 - 0.14X_3 + 0.097X_4 - 0.16X_5 + 0.036X_6 + 0.116X_7 \quad b_{\text{sig}} = 0.027; \quad (2)$$

$$Y_3 = 27.99 + 7.64X_1 + 9.11X_2 + 8.25X_3 - 4.25X_4 - 1.092X_5 - 1.087X_6 + 3.81X_7 \quad b_{\text{sig}} = 0.95; \quad (3)$$

TABLE 1 INFLUENCING FACTORS AND THEIR LEVELS OF VARIATION

CODE	FACTOR	LOW LEVEL (-)	HIGH LEVEL (+)
X_1	$\text{Fe}_2(\text{SO}_4)_3$ concentration, g/L	2	3
X_2	Temperature of $\text{Fe}_2(\text{SO}_4)_3$ solution, °C	40	50
X_3	pH of $\text{Fe}_2(\text{SO}_4)_3$ solution	1.7	1.9
X_4	Na_2SO_4 concentration, mg.equiv./L	0.01	0.02
X_5	Bubbling air speed, L/min	0	1
X_6	AV-17(Cl) mass, g	0.2	0.4
X_7	Contact duration of polymer AV-17(Cl) with solution, h	5	7

TABLE 2 MATRIX OF THE EXPERIMENTAL DESIGN

X_1	X_2	X_3	X_4	X_5	X_6	X_7	Y_1	Y_2	Y_3	Y_4	Y_5	Y_6	Y_7	Y_8	Y_9
+	+	+	+	+	+	+	51.18	0.61	50.55	0.046	0.58	6.25	0.0102	0.005	0.018
-	+	+	-	-	-	+	47.88	0.076	47.79	0.051	1.42	7.075	0.0127	0.0104	0.029
+	-	+	-	+	-	-	35.37	0.0	35.37	0.075	3.68	7.0	0.0204	0.0102	0.029
-	-	+	+	-	+	-	11.26	0.0	11.26	0.022	1.86	7.175	0.0083	0.0026	0.0085
+	+	-	-	-	+	-	37.56	0.83	36.77	0.034	0.63	6.375	0.0102	0.0	0.0165
-	+	-	+	+	-	-	13.32	0.0	13.32	0.044	2.19	7.0	0.0165	0.0	0.017
+	-	-	+	-	-	+	20.89	1.047	19.84	0.032	1.87	7.075	0.0204	0.0	0.017
-	-	-	-	+	+	+	9.045	0.0	9.045	0.021	1.103	6.95	0.0083	0.005	0.0085

$$Y_4 = 0.0406 + 0.0061X_1 + 0.0079X_3 - 0.00461X_4 + 0.0059X_5 - 0.0099X_6. \quad b_{\text{sig}} = 0.0045; \quad (4)$$

$$Y_5 = 1.66 - 0.46X_2 + 0.22X_3 + 0.22X_5 - 0.62X_6 - 0.42X_7. \quad b_{\text{sig}} = 0.18; \quad (5)$$

$$Y_6 = 6.86 - 0.18X_1 - 0.18X_2 - 0.0625X_5 - 0.175X_6. \quad b_{\text{sig}} = 0.039; \quad (6)$$

$$Y_7 = 0.0134 + 0.00195X_1 - 0.00413X_6 - 0.00475X_7. \quad b_{\text{sig}} = 0.0014; \quad (7)$$

$$Y_8 = 0.0042 + 0.0029X_3 - 0.0023X_4. \quad b_{\text{sig}} = 0.00166; \quad (8)$$

$$Y_9 = 0.018 + 0.0022X_1 + 0.0022X_2 + 0.0032X_3 - 0.0029X_4 - 0.0051X_6. \quad b_{\text{sig}} = 0.00044. \quad (9)$$

As expected, the increment of $\text{Fe}_2(\text{SO}_4)_3$ concentration (X_1), temperature (X_2), solution pH (X_3) and duration of polymer contact with solution (X_7), increase the Fe(III)-cations sorption (Eq.(3)) and the total content of iron in the polymer phase (Eq.(1)). The influence of X_1 , X_2 , X_3 and X_4 factors on iron-cations sorption by AV-17(Cl) (Eq.1), correlates perfectly with the data in the Ref.. The observed strong positive effect of temperature (X_2), supports the conclusion that the retention of metallic cations by the polymer is a chemical process and not a physical one. It is important to note that the speed of air bubbling through solution of $\text{Fe}_2(\text{SO}_4)_3$ (X_5 in Eqs.(1), (3)) significantly and negatively affects the metallic cations sorption. It means that the air contributes to the destruction of the Fe(III)-containing compounds in the polymer phase. The destruction of the metallic compounds takes place due to the redox processes. As a result of these processes a part of Fe^{3+} cations is reduced to Fe^{2+} . A part of Fe^{2+} cations passes in solution of $\text{Fe}_2(\text{SO}_4)_3$, and the other remain in the polymer phase as mobile cations into $\text{Fe}[\text{Fe}_3(\text{OH})_6(\text{SO}_4)_2]_2$ structures. The influence of factors on the Fe^{2+} cations content in the polymer phase is shown in Equation (2). Increment of $\text{Fe}_2(\text{SO}_4)_3$ and Na_2SO_4 concentration, of temperature, mass of polymer and contact duration of the polymer with solution (X_1 , X_2 , X_4 , X_6 , X_7), influence positively the Fe^{2+} ions content in the polymer phase, but factors X_3 and X_6 influence it negatively. The negative influence of pH and speed of bubbling air through the solution was explained by the oxidation by air oxygen a part of Fe^{2+} ions to Fe^{3+} . In water, the nitrogen compounds NO_x form acids HNO_2 and HNO_3 . The content of the NO_2^- ions (HNO_2) in water (recipient 4 in Figure 2) is quite small (Tab.2). The influence of factors on the content of NO_2^- ions in water is given by Equation (4). The assessment of the influence of factors on the formation of NO_2^- ions is very relative because

NO and NO_2^- are chemically unstable in presence of the oxygen and in the acid medium.

As shown in Equation (5), the air bubbling through the solution of $\text{Fe}_2(\text{SO}_4)_3$ leads to increasing NO_3^- ions content in water, but increment of temperature, influences it negatively. These data confirm the involving of air in the redox processes taking place in the system, containing polymer AV-17 and $\text{Fe}_2(\text{SO}_4)_3$ solution. The increase of the pH of $\text{Fe}_2(\text{SO}_4)_3$ solution (X_3), influences positively the content of NO_3^- in water (Eq.5) and Fe^{3+} in the polymer phase (Eq.3). The more the iron content is in the polymer phase, the greater the amount of nitrate ions in water is. The negative effect of the contact time of the polymer with $\text{Fe}_2(\text{SO}_4)_3$ solution on content of NO_3^- ions in water (X_7 in Eq.5) may seem incredible. But this effect can be explained by the fact that when air passes through the system (Fig.2) a part of NO_x and HNO_3 is released into the atmosphere. The initial pH of water (50 ml) in the recipient (Fig.2) is 9.0.

When air passes through the system, pH of water decreases (Tab.2). Partially the decrease of pH is due to CO_2 from air. The factor X_5 should not affect the pH of the water because air has passed through it in all experiments. However, as seen in Equation (6), factor X_5 influences the pH of the water, meaning that the decreasing pH of water is not only due to CO_2 from the air, but also the production of acid in it. In the solution of $\text{Fe}_2(\text{SO}_4)_3$, some NO_2^- and NO_3^- ions have been detected (Tab.2) and degree of the influencing factors is shown in Eqs.(7)-(9).

The content of NO_3^- ions in water (Y_5) has been optimized. In the conditions of $X_1=2.5$ g $\text{Fe}_2(\text{SO}_4)_3/\text{L}$; $X_2 = 0$ °C; $X_3 = 2.0$; $X_5 = 1.0$ L/min; $X_6 = 0.25$ g; $X_7 = 7$ h in the recipient was found 3.93mg NO_3^-/g ; implying that the experiments and regression equations are valid.

Conclusions

In the systems containing strongly basic cross-linked ionic polymer and $\text{Fe}_2(\text{SO}_4)_3$ solution unusual and complicated processes can take place. Besides anion exchange, in the systems other uncontrolled processes have occurred which can lead to unexpected results. These are the formation in the polymer phase of ultrafine particles of inorganic compounds and redox process. The redox processes taking place in the systems containing polymer, $\text{Fe}_2(\text{SO}_4)_3$ solution and air, lead to destruction of metallic compounds (jarostes) in the polymer phase and generation of Fe^{2+} ions and nitrogen compounds (NO_x). In the aqueous medium

these oxides turn into HNO_2 and HNO_3 .

The increment of the concentration of $\text{Fe}_2(\text{SO}_4)_3$ and Na_2SO_4 in solution, also of temperature, mass of polymer and contact duration of the polymer with solution contributes to the increasing Fe^{2+} ions content in the polymer phase. The air bubbling through the solution of $\text{Fe}_2(\text{SO}_4)_3$ contributes to the destruction of the Fe(III)-containing compounds in the polymer phase and lead to increasing NO_3^- ions content in water. The increment in temperature of the system containing strongly basic cross-linked ionic polymer and $\text{Fe}_2(\text{SO}_4)_3$ solution, influences negatively the NO_3^- ions formation. The more the iron content is in the polymer phase, the greater the amount of nitrate ions in water is. The problem of the occurrence of nitrogen compounds in the system remains to be solved in the nearest future.

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Vasile Gutsanu was born in Shendreni, Moldova in 1944. In 1970 he was graduated at Chisinau State University, Chemistry Faculty, Department of Physical Chemistry. In 1974 he was awarded a PhD degree, and in 1993 the degree of doctor habilitate and professor in physical chemistry. Many years he worked as researcher and a lecturer in the Institute of Chemistry of Academy of Sciences, Agricultural University and Technical University of Chisinau. Now he is working at Moldova State University as a professor. Area of expertise: Sorption of substances by ion exchangers, metal-organic complexation with electron – donor groups of cross-linked ionic polymers, polymers modified with metallic compounds, obtaining of nanoparticles of the metallic compounds in the polymer phase, obtaining of new selective sorbents and catalysts, Ecological Chemistry, water and gases purification. He is the author of eight books, the last being "Unusual processes on ion exchangers" (in Romanian) and "Secondary processes on ion-exchanging polymers".